Estuarine, Coastal and Shelf Science 166 (2015) 199–208

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

journal homepage: www.elsevier.com/locate/ecss

Occurrence of aragonite corrosive water in the North Yellow Sea, near the Yalu River estuary, during a summer flood

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ARTICLE INFO

Article history:
Accepted 18 February 2015
Available online 26 February 2015

Keywords:
$CaCO_3$ saturation state
Yalu River estuary
North Yellow Sea
coastal process

ABSTRACT

To understand seawater $CaCO_3$ saturation state (Ω_{arag} for aragonite and Ω_{cal} for calcite) dynamics in river-dominated ocean margins, we investigated the carbonate system and ancillary parameters in the North Yellow Sea, near the Yalu River estuary, during and after a summer flood (August and September 2013, respectively). During the flood period, nearshore Ω_{arag} ranged from 0.76 to 1.61 and Ω_{cal} ranged from 1.22 to 2.53. Aragonite undersaturation values were associated with quite low salinity of 14.58–25.18 and a broad dissolved oxygen saturation range from 58% to 102%. A week after the flood period, aragonite undersaturated waters together with the estuarine plumes disappeared. Based on field data analyses and simplified model simulation, we suggest that net community respiration/remineralization and the dilution of riverine water discharge both contributed to the low $CaCO_3$ saturation states.

1. Introduction

Both calcium and carbonate ions are essential for many marine organisms to form calcium carbonate ($CaCO_3$) skeletons and shells. The potential of seawater to promote or corrode these $CaCO_3$ shells and skeletons is measured via the $CaCO_3$ saturation state (Ω), which is defined as the product of calcium and carbonate ion concentrations divided by the apparent solubility product (K_{sp}^*) for either aragonite or calcite, i.e., $\Omega_{arag} = [Ca^{2+}] \times [CO_3^{2-}]/K_{sp}{}^*{}_{arag}$ or $\Omega_{cal} = [Ca^{2+}] \times [CO_3^{2-}]/K_{sp}{}^*{}_{cal}$. $\Omega_{arag} > 1$ or $\Omega_{cal} > 1$ indicates that the $CaCO_3$ mineral is stable in the seawater, while $\Omega_{arag} < 1$ or $\Omega_{cal} < 1$ indicates that aragonite or calcite is unstable. Without protective mechanisms, calcifying organisms such as corals and shellfish are vulnerable to $CaCO_3$ undersaturated seawaters with $\Omega_{arag} < 1$ or $\Omega_{cal} < 1$ (Feely et al., 2002; Yamamoto et al., 2012).

Usually the concentration of seawater calcium ions depends on salinity, while the availability of carbonate ions is controlled by the reaction of CO_2 with the seawater carbonate system. In response to increasing atmospheric CO_2, sea surface Ω inevitably decreases and its potentially negative effects on marine organisms and ecosystems have received considerable attention in recent years (Doney et al., 2009; Yamamoto-Kawai et al., 2009; Feely et al., 2012; Yamamoto et al., 2012). However, coastal oceans respond to this CO_2 problem differently to that of open oceans (Borges and Gypens, 2010; Cai et al., 2011; Sunda and Cai, 2012; Zhai et al., 2012; Duarte et al., 2013). They are more vulnerable to the potentially negative effects of ocean acidification, as very low sea surface and/or near surface Ω_{arag} and Ω_{cal} values may periodically occur in some coastal zones due to upwelling of CO_2-rich water (Feely et al., 2008; Barton et al., 2012; Gruber et al., 2012) and/or metabolic processes with CO_2 release (Feely et al., 2010; Mathis et al., 2011; Zhai et al., 2014).

In many coastal zones, mixing with fresh water affects seawater Ω dynamics (Salisbury et al., 2008; Jiang et al., 2010; Chou et al., 2013). Fresh water intrusions not only decrease salinity but also total alkalinity (TAlk) and dissolved inorganic carbon (DIC), thereby diminishing both carbonate ion concentrations and Ω values (Salisbury et al., 2008; Yamamoto-Kawai et al., 2009; Jiang et al., 2010; Sunda and Cai, 2012). Nonetheless, how fresh water dilutions act with natural or anthropogenic CO_2 additions to affect Ω dynamics has rarely been studied (Sunda and Cai, 2012). In this study, we investigated the carbonate system and ancillary parameters in the North Yellow Sea (NYS) during and after a summer flood. We also quantificationally examined combined effects of CO_2 additions and fresh water dilutions on northern NYS Ω dynamics. Our dataset provides an opportunity, for the first time, to understand Ω dynamics in the river-dominated ocean margin near the Yalu River estuary (Fig. 1).

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http://dx.doi.org/10.1016/j.ecss.2015.02.010
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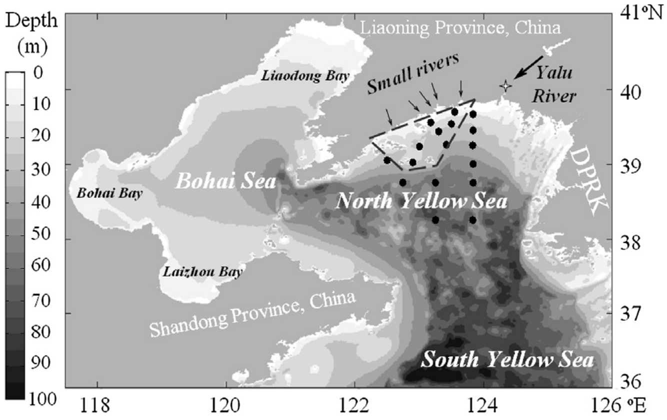

Fig. 1. North Yellow Sea and sampling sites. A coastal marine aquaculture zone is enclosed within the dashed lines. Arrows along the north coast indicate Yalu River and several small rivers. The star symbol indicates the Huang-gou hydrological station. DPRK = Democratic People's Republic of Korea.

2. Materials and methods

2.1. Study area and hydrological background

The NYS is a shallow marginal sea of the western North Pacific, surrounded by the Liaoning and Shandong Provinces of China and the Democratic People's Republic of Korea. Its summer hydrography is characterized by a subsurface cold water mass (Miao et al., 1991; Zhao, 1996; Zhai et al., 2014). The rain-bearing southwest monsoon lasts from June to September (Zhai et al., 2014), feeding several small seasonal rivers along the coastline of the northern NYS (Fig. 1). In the flood season, freshwater discharge from Yalu River and other rivers may affect the coastal ecosystem, where marine bivalve species (calcifying organisms) such as scallops and clams are of major ecological and economic importance (Fig. 1). Algae blooms frequently occur in the NYS from spring to autumn (Zhang, 1994; Zhai et al., 2014). As a result, biogenic particles sink into deeper waters (usually below 25 m depth), where they consume dissolved oxygen (DO) and release CO_2. The accumulated CO_2 leads to very low subsurface water Ω_{arag} values of 1.13–1.40 in autumn (State Oceanic Administration of China, 2013; Zhai et al., 2014).

In July and August 2013, Liaoning Province, close to the area under study, experienced exceptionally heavy rainfall. As recorded by the Liaoning Provincial Department of Water Resources (http://www.dwr.ln.gov.cn/), regional rainfall averages were ~400 mm in July and ~120 mm in August in the eastern and southern parts of Liaoning Province. Consequently, water discharge from the lower Yalu River increased from <1600 $m^3 s^{-1}$ before 15 July to 4000–5140 $m^3 s^{-1}$ in late July (data from Huang-gou, the farthest major downstream hydrological station in Yalu River, Fig. 1). Moreover, high water fluxes of 2000–5000 $m^3 s^{-1}$ dominated in August, with a short-term break in mid-August (see the supplement Fig. S1). Note that water flow in the lower Yalu River usually varies little within a narrow range of 1000 ± 250 $m^3 s^{-1}$ (Zhai et al., 2014), which is modulated by the manipulation of water discharge from several major dams (including Sup'ung, Yunfeng, Weiyuan, and Taipingwan). Therefore, the significant water discharge events in the lower Yalu River (e.g., persistent water flux from 3280 to 5140 $m^3 s^{-1}$ from 25 July to 8 August) were partially human-designed (http://www.dwr.ln.gov.cn/20137/content_93501_24.htm). After 31 August, the water flow in the lower Yalu River finally dropped to its usual value of ~1000 $m^3 s^{-1}$ (see the supplement Fig. S1).

2.2. Sampling and analyses

Two surveying cruises were conducted in the northern NYS from 31 July to 3 August 2013 (during a flood period) and from 5 to 8 September 2013 (a week after the flood in late August). During each cruise, 17 grid stations were sampled (Fig. 1) for seawater DO, dissolved inorganic carbon (DIC), and total alkalinity (TAlk) analyses. Water samples were collected at three or four different depths (including 2 m and bottom level) using 2-L Niskin bottles mounted with a calibrated Conductivity-Temperature-Depth/Pressure (CTD) unit (SBE-19 plus, Sea Bird Co.). The associated salinity (Practical Salinity Scale of 1978) and in situ temperature were obtained from the SBE-19 plus CTD. The DO data were collected on board following the classic Winkler titration procedure, with an uncertainty level of <0.5% (Zhai et al., 2012). DO saturation was calculated from field-measured DO concentrations divided by DO concentration at equilibrium with the atmosphere. The latter was calculated from temperature, salinity and local air pressure, as per the Benson and Krause (1984) equation. To obtain a quantificational view of metabolism processes, we also calculated apparent O_2 deficit (similar to the apparent oxygen utilization or AOU defined by oceanographers) via the air-equilibrated DO concentration minus the field-measured DO concentration. Ignoring effects of air-sea exchanges and water mixing, a positive O_2 deficit value means net community respiration and/or remineralization, while a negative O_2 deficit value indicates net community production.

Following Zhai et al. (2014), water samples for DIC and TAlk analyses were stored in 60 mL borosilicate glass bottles (for DIC, bubble free) and 140 mL high-density polyethylene bottles (for TAlk). They were immediately mixed with 50 μL of saturated $HgCl_2$, and then sealed and preserved at room temperature until determination. Based on Huang et al. (2012) results, there were no differences between the measurement results from our procedure and those from the Dickson et al. (2007) sampling procedure.

Both DIC and TAlk samples were unfiltered, but were allowed to settle before measurement. Data were collected within time frames of 20 days (August data) and 70 days (September data) upon sampling, using commercial analytical systems (models AS-C3 and AS-ALK2, Apollo SciTech Inc., USA). Briefly, DIC was measured by infrared detection following acid extraction of a 0.5 mL sample with a Kloehn® digital syringe pump, as described in Cai et al. (2004). TAlk was determined at 25.0 °C by Gran acidimetric titration on a 25 mL sample with a Kloehn® digital syringe pump, as described in Cai et al. (2010), using a precision pH meter and an Orion® 8102BN Ross electrode for detection. To ensure the measuring quality of DIC and TAlk, certified reference materials from Andrew G. Dickson's laboratory (Scripps Institute of Oceanography, U.S.A.) were regularly checked at a precision of ±2 $\mu mol\ kg^{-1}$.

2.3. Calculating other carbonate system parameters from DIC and TAlk

Seawater fugacity of CO_2 (fCO_2), pH_T (the negative logarithm of the total concentration of H^+ and HSO_4^- ions), concentrations of carbonate ion, Ω_{arag} and Ω_{cal} were calculated from the DIC, TAlk, seawater temperature, and salinity values using the program CO2SYS.xls (Pelletier et al., 2011), an updated version of the original CO2SYS.EXE (Lewis and Wallace, 1998). The dissociation constants for carbonic acid were those determined by Millero et al. (2006), and the dissociation constant for the HSO_4^- ion was determined as per Dickson (1990). The K_{sp}* values for aragonite and calcite were taken from Mucci (1983), and the Ca^{2+} concentrations were assumed to be proportional to salinity, as presented in Millero (1979).

To further assess the quality of the carbonate data, we also calculated pH data at 25 °C from DIC and TAlk values. These data